CERTIFICATION OF TRANSLATION

I, BANHOLZER Vivien, of CABINET PLASSERAUD, 84, rue d'Amsterdam, 75440 PARIS CEDEX 09, FRANCE, do hereby declare that I am well acquainted with the French and English languages, and verify that the document attached is a true English language translation of the text of International Patent Application no. PCT/FR00/02197.

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STOPPER INCORPORATING A COMPOSITION OR PREBLEND BASED ON VOLATILE CORROSION INHIBITORS

The invention relates to polymer-based stoppers, one of the components of which consists of a composition or preblend based on volatile corrosion inhibitors.

The invention also relates to the use of the abovementioned stoppers for the internal protection of hollow metal components against corrosion.

In the present invention, the term "stopper" means any component capable of obstructing the opening of a hollow component, such as stoppers, capsules, threaded bodies, used for the localized volatile anti-corrosion protection of certain hollow internal parts of metal components.

The material constituting the polymer-based stoppers, one of the components of which consists of a composition or preblend based on volatile corrosion inhibitors, has been used to prepare wrapping articles.

Specifically, it is known practice to use volatile corrosion inhibitors when it is a matter of protecting against the corrosion of corrosion-sensitive metal components, in particular those made of mild steel with a low carbon content and which, once machined, are dispatched in their given form to their place of destination in a shipping container for the purpose of finishing on site, in particular by painting; the risks of corrosion are thus considerable, especially when the components in question are sent to hot and humid regions.

For example, when the metal components to be protected are wrapped in films, VCIs are incorporated into the material constituting these films; given that these films can come into direct contact with the surface of the components to be protected, corrosion inhibitors which act by contact are also incorporated into the mass constituting these films.

Under these conditions, volatile corrosion inhibitors offer very good protection against corrosion

and have the advantage of making it possible to avoid the use of conventional techniques for protecting metal components; these conventional techniques consist in applying paints, varnishes, plastics, waxes, greases and oils, which should be removed before the on-site finishing, thus entailing additional costs and pollution.

Volatile corrosion inhibitors, generally referred to as VCIs, incorporate additives whose vapour pressure can be considered as non-negligible at the working temperature (for example from about 10^{-5} to 10^{-1} mmHg, at 20°C), and which are capable of inhibiting the corrosion of metals.

These VCIs act by virtue of the fact that they are conveyed in vapour form to the metal surface to be protected, in order to be adsorbed thereon or dissolved in condensation water, if any.

Products are also known which are classified by extension in VCIs on account of the fact that one of their reaction products has an adequate vapour pressure. Thus, for example, sodium nitrite, in the presence of ammonium ions, can form ammonium nitrite which is relatively volatile. The starting sodium nitrite is thus considered as a VCI.

It is occasionally necessary to corrosion-protect only the internal parts of large-sized hollow metal components of complex geometry, in particular cavities, threaded parts or tubular holes. Stoppers in accordance with this invention, based on polymers and optionally on other structuring agents, shaped by the usual techniques of the polymer industry (extrusion, injection-moulding, thermoforming) make it possible to obstruct the openings of the metal components and provide them with the required localized protection, thus considerably minimizing the costs.

In order to incorporate VCIs into the material constituting wrappings, in particular films which are often based on thermoplastic polymers, it is known practice to prepare direct mixtures of VCI powders with

the polymers and to form the articles in question directly by extrusion or injection-moulding.

At the extrusion temperature, which is about 160°C for low-density polyethylene and 240°C for polypropylene, VCIs are extremely volatile, and this leads, in the case of articles of low thickness, to the appearance of high porosity and to a strong risk of degradation and/or decomposition with removal of at least some of the VCIs. The efficacy from the point of view of the anticorrosion of such articles is thus greatly reduced as a result of the loss of active material.

To overcome this drawback, i.e. to limit the loss of VCIs during the actual preparation of the articles, it has been proposed to provide preblends containing VCIs, i.e. concentrates of active material dispersed in supports such as polymers, solvents and plasticizers; polymer-based preblends (patent BR-A-9001035) have the general advantage of being homogeneous and easy to handle; these preblends are then incorporated into the polymers for the purpose of preparing articles.

Given, however, that the temperatures used at the time of preparation of the preblends are often greater than 150°C, at least partial degradation of the said preblends occurs; thus, for example, it is noted that dicyclohexylamine nitrite, mixed and extruded with polyethylene at 160°C, gives preblend granules which have a dark yellow colour, characteristic of extensive degradation, i.e. a loss of activity.

To avoid these excessive thermal degradations, it has been proposed to use liquid preblends, based on oil, which do not need to be taken to high temperatures during their manufacture (patent US-A-4 913 874).

However, given that VCIs are rarely soluble in these oily media, this results in heterogeneity of the preblends obtained and the occurrence of difficulties due to local superconcentrations or under-

concentrations during their subsequent incorporation into the polymers from which the articles are made.

It has also been proposed to overcome this drawback by using liquid preblends in the form of solvent-based or oily solutions comprising the VCIs, these preblends not being incorporated during the extrusion, but applied to films by spraying, thus forming, after evaporation of the solvent, either a powdery layer of VCI (patent DE 3 417 149 A1) or an oily layer containing the VCIs (patent GB 2 188 274 A).

The drawback of these preblends lies in the fact that the VCIs are not imprisoned in a matrix imposing slow release, and the protection obtained is thus short-lived. Moreover, the adhesion of the layers deposited onto the articles is low and leads to losses during manipulation and to the need to clean the components that are to be protected, which is precisely what one would wish to avoid.

The aim of the invention is to provide stoppers based on polymers using at least one VCI-based composition, which satisfy the various practical requirements better than those already existing.

An object of the invention is also to propose novel uses for these VCI-based stoppers, such as the partial and localized protection of certain internal parts of hollow metal components.

Following extensive research, the Applicant Company has now, to its credit, found that these aims can be achieved if stoppers are used based on polymers incorporating a composition based on volatile corrosion inhibitors which comprises structuring agents capable of allowing the preparation of a preblend at temperatures that are low enough to limit the release and/or degradation of these VCIs as much as possible during this preparation.

Consequently, the polymer-based stoppers in accordance with the invention are characterized in that they incorporate a composition based on volatile corrosion inhibitors which comprises an effective

amount of at least one structuring agent, consisting of a solid or pasty substance whose melting point is from 40 to 110°C, preferably from 50 to 90°C, by means of which the release and/or degradation of the VCIs at the time of formation of the composition or preblend is limited as much as possible.

According to one advantageous embodiment, the composition used in the stoppers in accordance with the invention comprises from 1 to 90%, preferably from 20 to 60%, by weight of at least one volatile corrosion inhibitor and from 10 to 99%, preferably from 40 to 80%, of at least one structuring agent consisting of a solid or pasty substance whose melting point is from 40 to 110°C, preferably from 50 to 90°C.

According to another advantageous embodiment, the composition used in the stoppers in accordance with the invention comprises at least one structuring agent chosen from the group comprising solid or pasty, aliphatic and/or resinous compounds with a low melting point of between 40 and 110°C, preferably between 50 and 90°C.

According to another advantageous embodiment of the composition used in the stoppers according to the invention, the structuring agent is chosen from the group comprising mono- or polyfunctional aliphatic organic compounds which are linear and/or slightly branched with hydrocarbon-based chains containing at least 10 carbon atoms, including, in particular:

- saturated or unsaturated, optionally oxidized mono- or dicarboxylic acids, their esters and their salts,

- phosphoric, sulphonic and phosphonic acids, their esters with alcohols and their alkali metal, alkaline-earth metal, zinc, aluminium and/or organic amine salts,

- cyclic or acyclic compounds of the group comprising lactones, ketones, aldehydes, amides and acetals,

- optionally polyalkoxylated, cyclic or acyclic, primary or secondary higher alcohols with a hydrocarbon-based chain containing at least 10 carbon atoms,

- linear and/or slightly branched aliphatic hydrocarbons, in particular paraffins and isoparaffins,

- polyolefins and their copolymers with low molecular masses from 3000 to 20,000 g/mol,

- polyglycols, in particular polyethylene glycols of molecular mass from 2000 to 10,000 g/mol.

According to another advantageous embodiment of the composition used in stoppers in accordance with the invention, the structuring agent is chosen from the group comprising resinous compounds with a polymeric and/or cyclic structure and which can contain, in minor proportion, aromatic derivatives and cyclic terpenes.

According to another advantageous embodiment of the composition in accordance with the invention, the structuring agent is chosen from the group of those identified in Table A below, some of which are waxes or oils of natural or synthetic origin.

TABLE A

Origin of the structuring agent	Majority chemical nature of the structuring agent	Name of the structuring agent	Melting point (°C)	Density at 25°C ASTM D 1298	Penetration index at 25°C ASTM D 1321
Natural	ester (myricyl cirotate)	Carnauba	83-86	0.995	-
	ester (myricyl palmitate)	beeswax	62-65	0.955	-
Mineral	paraffinic hydrocarbons (mixture)	paraffin	50-60	0.900	15

	isoparaffinic and naphthenic hydrocarbons	micro-crystalline wax	69	0.930	29
	aliphatic hydrocarbons (mixture)	petrolatum	70-72	0.910/20°C	43-45
Synthetic	polyethylene	polyethylene wax	88	0.930	6.5
	oxidized isoparaffinic hydrocarbons	oxidized micro-crystalline wax	85	-	13
	phosphoric ester of C_{16}/C_{18} fatty alcohols	-	83-89	0.998	-
	polyethylene glycol	polyethylene glycol 4000	57-59	1.112/99°C	-

According to another advantageous embodiment, the composition used in the stoppers in accordance with the invention comprises at least one volatile corrosion inhibitor chosen from the group comprising:

- nitrogenous derivatives and in particular, firstly, aliphatic, aromatic, acyclic or cyclic amines including dicyclohexylamine, cyclohexylamine, morpholine, diisopropylamine and benzylamine, their organic salts including the benzoates, carbamates, laurates, caprylates and succinates, or their inorganic salts including the nitrites, nitrates, carbonates, phosphates and phosphites, and, secondly, heterocycles including imidazole and its derivatives, triazoles and their derivatives, as well as hexamethylenetetramine,
- nitrogenous oxido derivatives including the alkali metal or alkaline-earth metal salts of nitrous acid, and
- benzoic derivatives of these metals, such as sodium benzoate.

It is possible to include in the composition used in the stoppers in accordance with the invention

and/or in the stoppers one or more adjuvants chosen from the group comprising:

- antioxidants and/or degradation inhibitors including bisphenol A, butyl-hydroxytoluene, di-tert-butyl phosphite, trinonyl phenoxyphosphite and dilauryl thiodipropionate,

- anti-UV absorbing agents including benzotriazoles, triazines, hydroxybenzophenones and radical inhibitors including SHAs or Sterically Hindered Amines and HALS "Hindered Amine Light Stabilizers",

- external antistatic agents including phosphoric ethers of ethoxylated alcohols and ethoxylated amine chlorides, or internal antistatic agents including ethoxylated fatty amines, ethoxylated polyols and alkyl sulphonates,

- external or internal lubricants including paraffins, fatty alcohols, fatty acids, esters of fatty alcohols and acids, and amides,

- plasticizers including dioctyl phthalate, tricresyl phosphate and diesters of aliphatic acids,

- inorganic pigments including $PbSO_4$, $PbCrO_4$, CdS.ZnS, organic pigments including azo derivatives, phthalocyanins or anthraquinones, and

- flame retardants including bromo and chloro phosphorus compounds, hydrides of Al, Mg and Zn compounds, as well as epoxy oligomers,

- mineral fillers including chalks and carbonates, talcs, clays and silicas.

These adjuvants can also be added solely at the time of the incorporation of the composition into the polymer from which the stoppers in accordance with the invention are manufactured, or into the structuring agent from which the stoppers in accordance with the invention are manufactured.

These stoppers are characterized in that at least one of their components consists of a composition described above and in that they are prepared from at

least one polymer which constitutes at least 50% of their weight.

The abovementioned polymers which constitute at least 50% of the mass of the stoppers in accordance with the invention can be chosen from those of the group comprising:

- polyolefins including polyethylenes, polypropylene, polybutene and their copolymers with one or more unsaturated monomers including vinyl acetate, acrylic acid and its esters with carbon-based short-chain alcohols,
- polyvinyl chloride and its copolymers, acrylic copolymers and their derivatives, and
- polyamides, polystyrenes, polycarbonates, polyesters, polyurethanes, rubbers including natural rubber, styrene-butadiene and polychloroprene.

The process for preparing these stoppers generally comprises, successively, a step of preparation of a composition or preblend based on volatile corrosion inhibitors in accordance with the invention and a subsequent step during which the preblend is incorporated into one of the abovementioned polymers, the stoppers being obtained in particular by extrusion, moulding, injection-moulding or thermoforming from the blend comprising the preblend and the polymer.

The stoppers are used for protecting the internal parts of hollow metal components that are sensitive to corrosion, during their transportation or storage, without an additional protective treatment being applied to these components.

The invention may be understood more clearly with the aid of the non-limiting examples which follow, and which concern advantageous embodiments.

EXAMPLE 1

For the preparation of a VCI, 70 g of sodium nitrite, 17.5 g of benzotriazole and 12.5 g of ammonium benzoate are mixed together and then micronized in an

air-jet micronizer to give 100 g of homogeneous powdery mixture referred to as [1a] and having an average particle size of between 1 and 15 µm; this powder constitutes a VCI.

In a heating tank fitted with a rotating stirrer and scraper, 226 g of the paraffin defined in Table A are melted at 65°C, after which 100 g of powder [1a] are incorporated into the molten mass and carefully dispersed.

2 g of anti-UV agent (sold under the brand name Tinuvin 622 LD by Ciba Geigy), 2 g of antioxidant - degradation inhibitor (sold under the brand name Chimassorb 944 LD by Ciba Geigy) and 3 g of yellow dye Colour Index PY10401/70, are then added.

The dispersion is prepared with stirring at a speed of between 300 and 500 rpm, for 10 minutes.

The 333 g of the mixture thus obtained, which constitutes a preblend [1b], are poured for cooling onto a laboratory flaking machine maintained at 10°C, and are then cut into flakes of between 0.5 and 10 mm in size.

300 g of preblend [1b] are homogeneously cold-blended with 5.7 kg of low-density polyethylene ($d=0.925$ g/cm^3 and melt index MI=20 g/10 minutes); the mixture obtained is injected at a temperature ranging between 145 and 160°C into a mould whose nest is cooled to 40°C, mounted on a Krauss Maffei series C - 40 t injection-moulding machine, with hydraulic closure (400 kN) and which works at a rate of 30 beats/minute; the residence time of the molten material in each of the six zones of the cylinder is 15.6 seconds.

The finished article obtained is yellow VCI capsules, referred to as [1c], with a diameter of 20 mm, a thickness of 1 to 3 mm and a mass of 1 g, which are used for protecting the cavities and threaded parts of motor vehicle engines.

The volatile anti-corrosion efficacy of these VCI capsules [1c] was tested on mild steel test pieces, in the form of pins; the test used involves two

capsules and corresponds to US standard FED-STD 101, method 4031B.

This test method consists in placing a steel pin in a confined atmosphere charged with VCI released from the film, and then in bringing about, by controlled cooling, condensation at the surface of the pin in order to bring about a possible oxidation after a determined time. The degree of rusting indicates the anti-corrosion efficacy of the stopper with regard to the material constituting the pin.

After this test, it is found that the steel pin protected with the corrosion-inhibiting vapours which are released from the two VCI capsules [1c] shows no oxidation on its surface.

The same test was carried out, for comparative purposes, using "control" capsules, referred to as [1d], which are identical in all respects to the capsules [1c], except for the fact that they contain no VCI [1b] identified above; the 100 g of powder [1a] forming part of the composition of the preblend [1b] were replaced with 100 g of mineral filler based on calcium carbonate.

After the test, the pin protected with the control capsules [1d] is completely attacked: many blisters and rust are found over 100% of its surface.

EXAMPLE 2

For the preparation of a VCI, 300 g of preblend [1b] defined in Example 1 are homogeneously cold-blended with 5.7 kg of low-density polyethylene (d=0.925 g/cm^3 and melt index MI=20 g/10 minutes); the blend obtained is injected at a temperature ranging from 135 to 150°C into a mould whose nest is cooled to 40°C, melted on a Krauss Maffei series C - 40 t injection-moulding machine, with hydraulic closure (400 kN), working at a rate of 60 beats/minutes; the residence time of the molten material in each of the six zones of the cylinder is 9.9 seconds.

The finished article obtained is yellow VCI stoppers, referred to as [2c], with a diameter of 55 mm, a thickness of 1.5 mm and a mass of 6.5 g, which are used for protecting the cavities and threaded parts of motor vehicle engines.

The volatile anti-corrosion efficacy of these VCI stoppers [2c] was tested on mild steel test pieces, in the form of pins; the test used involves one third of the stopper, i.e. 2.2 g, and corresponds to US standard FED-STD 101, method 4031B, described in Example 1.

After this test, it is found that the steel pin protected with the corrosion-inhibiting vapours which are released from the VCI stopper [2c] shows no oxidation on its surface.

The same test was carried out, for comparative purposes, using a "control" stopper, referred to as [2d], which is identical in all respects to the stopper [2c], except for the fact that it contains no VCI [1b] identified above; the 100 g of powder [1a] which form part of the composition of the preblend [1b] were replaced with 100 g of mineral filler based on calcium carbonate.

After the test, the pin protected with control stopper [2d] is completely attacked: many blisters and rust are found over 100% of its surface.